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14. ABSTRACT The goal of this project was to obtain an atomic-scale understanding of the surface processes that underlie the growth by molecular beam epitaxy (MBE) of HgCdTe on As-passivated Si surfaces. It is generally recognized that in MBE the first few monolayers determine the quality and structure of the final crystalline film. In principle, the methods of surface science can provide the critically needed information about the initial stages of film growth. However, because of the volatile and toxic nature of As and CdTe, special equipment had to be constructed before the deposition processes could be studied. The resulting unique apparatus allowed us to deposit As and CdTe onto Si substrates in a separate preparation chamber with					
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Report Title

Final Report for "Surface Structure and Chemistry in the Epitaxial Growth of Cadmium Telluride on Silicon",
DAAD19-0202-0029

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The goal of this project was to obtain an atomic-scale understanding of the surface processes that underlie the growth by molecular beam epitaxy (MBE) of HgCdTe on As-passivated Si surfaces. It is generally recognized that in MBE the first few monolayers determine the quality and structure of the final crystalline film. In principle, the methods of surface science can provide the critically needed information about the initial stages of film growth. However, because of the volatile and toxic nature of As and CdTe, special equipment had to be constructed before the deposition processes could be studied. The resulting unique apparatus allowed us to deposit As and CdTe onto Si substrates in a separate preparation chamber with subsequent transfer under vacuum into the main analysis chamber. We used the apparatus to characterize As on several different Si surfaces with the techniques of scanning tunneling microscopy (STM), X-ray photoelectron spectroscopy (XPS), and Low Energy Electron Diffraction (LEED). The surface analyses were performed with instrumentation that was nearly twenty years old, which slowed progress due to the need for frequent and difficult repairs. Unanticipated budget cuts also impeded progress. Nevertheless, several conference presentations and publications resulted from this work.

List of papers submitted or published that acknowledge ARO support during this reporting period. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

C. Fulk, R. Sporken, J. Dumont, D. Zavitz, M. Trenary, B. Gupta, G. Brill, J. Dinan, and S. Sivananthan, "Arsenic Deposition as a Precursor Layer on Silicon (211) and (311) Surfaces", J. Electron. Mater. 34, 846-850 (2005)

Daniel H. Zavitz, Alexandra Evstigneeva, Rasdip Singh and Michael Trenary "Influence of arsenic on the atomic structure of the Si(112) surface", J. Electron. Mater. 34, 839-845 (2005).

C. Fulk, S. Sivananthan, D. Zavitz, R. Singh, M. Trenary, Y. P. Chen, G. Brill, and N. Dhar, "The Structure of the Si(211) Surface", J. Electron. Mater. 35, 1149-1454 (2006)

Number of Papers published in peer-reviewed journals: 3.00

(b) Papers published in non-peer-reviewed journals or in conference proceedings (N/A for none)

Number of Papers published in non peer-reviewed journals: 0.00

(c) Presentations

A. Evstigneeva, D. H. Zavitz, R. Singh, C. Fulk, G. Badano, S. Sivananthan, R. Sporken, and M. Trenary, "Surface Science Studies of Arsenic Passivated Silicon for Cadmium Telluride Film Growth", Oral presentation at the 2003 U.S. Workshop on the Physics and Chemistry of II-VI Materials, September 17-19, New Orleans.

Number of Presentations: 1.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts): 0

Peer-Reviewed Conference Proceeding publications (other than abstracts):

C. Fulk, R. Sporken, J. Dumont, D. Zavitz, M. Trenary, B. Gupta, G. Brill, J. Dinan, and S. Sivananthan, "Arsenic Deposition as a Precursor Layer on Silicon (211) and (311) Surfaces", J. Electron. Mater. 34, 846-850 (2005)

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(d) Manuscripts

Number of Manuscripts: 0.00

Number of Inventions:

Graduate Students

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
Alexandra Evstigneeva	0.50
Daniel Zavitz	0.50
Kumudu Mudiyansele	0.00
Eldad Herceg	0.00
Rasdi Singh	0.00
FTE Equivalent:	1.00
Total Number:	5

Names of Post Doctorates

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
Rasdi Singh	0.50
FTE Equivalent:	0.50
Total Number:	1

Names of Faculty Supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	National Academy Member
Michael Trenary	0.08	No
FTE Equivalent:	0.08	
Total Number:	1	

Names of Under Graduate students supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
FTE Equivalent:	
Total Number:	

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: 0.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:..... 0.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):..... 0.00

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The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense 0.00

The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields: 0.00

Names of Personnel receiving masters degrees

NAME

Total Number:

Names of personnel receiving PhDs

NAME

Rasdip Singh

Eldad Herceg

Kumudu Mudiyansele

Total Number:

3

Names of other research staff

NAME

PERCENT SUPPORTED

FTE Equivalent:

Total Number:

Sub Contractors (DD882)

Inventions (DD882)

Final Report for “Surface Structure and Chemistry in the Epitaxial Growth of Cadmium Telluride on Silicon”, DAAD 19-0202-0029

Michael Trenary
Department of Chemistry
University of Illinois at Chicago

Introduction

The goal of this project was to employ surface science methods to explore the atomic scale processes related to growth of crystalline HgCdTe films on silicon substrates by molecular beam epitaxy (MBE) [1]. Most previous surface science studies of the fundamentals of MBE growth have concentrated on materials most relevant to microelectronics, such as homoepitaxy of Si on Si, heteroepitaxy of Ge on Si, and the growth of GaAs and other III-V semiconductors [2]. Because the growth of II-VI semiconductors for infrared detector applications is of more limited interest, the problems unique to this field have not been adequately addressed in previous surface science studies. The large lattice mismatch between silicon and HgCdTe of 19% makes it difficult to achieve growth of epitaxial films with defect concentrations that are low enough for use in practical infrared focal plane array devices. Since HgCdTe can be grown on CdTe, obtaining a high quality CdTe layer is the major hurdle. Although a variety of novel strategies have been employed to achieve better quality films, through our interactions with the groups more directly involved in MBE growth of HgCdTe on silicon surfaces, it became clear that the substrates of most interest were clean and As-passivated Si(211) and our work focused on these surfaces.

The (211) and other high index silicon substrates have been the subject of previous detailed surface structural studies. There are several theoretical studies of the structure of Si(211) [3-5], but these have relied on often contradictory experimental studies implying that this surface forms stable but reconstructed surfaces. In contrast, a thorough survey using scanning tunneling microscopy (STM) by Baski, *et al.* [6] of a variety of high-index silicon surfaces has contradicted this assumption and has shown that while several high index silicon planes form stable surfaces, Si(211) is not among them. Instead, Si(211) is known to facet into stable (111) and (337) planes. The influence of arsenic deposition on the stability and structure of Si(211) has not been studied, even though this is an issue of ultimate importance for the MBE growth of CdTe onto this silicon substrate. On the Si(111) surface, arsenic is known to replace the topmost Si layer leading to a stable (1x1) surface instead of the usual 7x7 reconstruction [7]. There are thus two issues to consider with respect to the structure of As/Si(211): 1) How does the As influence the faceting characteristics of the clean surface? and 2) What is the influence of the arsenic on the atomic structure of the individual nanofacets of Si(211)? To address such questions, we have used the techniques of X-ray photoelectron spectroscopy (XPS), low energy electron diffraction (LEED), and STM to study the structure of the clean and As covered Si(211) surface. The ultimate goal of conducting such fundamental surface science studies of the atomic scale structure and processes that underlie the MBE growth of II-VI compounds on silicon substrates is to develop a more systematic and less empirical basis for improving the quality of the final product.

Experimental Issues

It was originally envisioned that we would use only existing instrumentation for the experimental work of this project. Specifically, an ultra-high vacuum chamber equipped for XPS, LEED, and STM was dedicated exclusively to this project. This apparatus was originally constructed with funding from AFOSR and DURIP in 1988 and has been used for numerous surface science studies. The focus of the proposed work was to use STM to obtain atomically-resolved images of Si surfaces, with and without an As passivating layer. Our STM was one of the first commercial ultra high vacuum instruments ever sold and our initial work with it was very successful and many high quality publications were obtained. However, the company that manufactured this STM soon discontinued support of it. Although my students and I were capable of routine repairs, soon after the start of this ARO grant a major problem with the electronics developed that we were unable to fix. It was beyond the capabilities of our own electronics shop, and no commercial vendor was interested in trying to fix it. Finally, after about one year of effort involving help from a talented graduate student in electrical engineering, we were able to get the instrument working again. In the meanwhile, we worked on experiments that could be done with the other instruments on the chamber. Although we had used our STM for studies of silicon surfaces and even for atomically resolved studies of deposited thin films in the past, the deposition of As and CdTe required the addition of a preparation chamber. Since no equipment funds were included in the budget of this grant, we did this by scavenging parts from other instruments and older equipment. A fair amount of effort was spent optimizing the use of the preparation chamber for the deposition of As onto Si surfaces, transferring the samples into the analysis chamber, and then characterizing the As/Si surfaces with XPS, LEED, and in the final period, with STM.

The instrumentation issues that plagued our efforts to achieve the quality and quantity of results we originally hoped for have now been largely solved through major new instrumentation purchases. These consisted of new electronics for our older STM, purchased from the company RHK. These are universal electronics designed to be compatible with scanning probe microscopes from a variety of vendors. The second major instrument acquisition was of a complete variable temperature STM system from Omicron. This was obtained at a bargain rate as a used instrument from Northwestern University. Both instruments would be available for future work in the area of STM studies of the sort originally planned. I now have a new generation of students trained on the use of these instruments. If another three-year grant dedicated to the same issues as the original grant were awarded, we would likely be able to achieve many of the goals of the previous grant.

Results

Many of our results have been described in three separate publications. Therefore only brief summaries of these results are given here. In addition, a student, Daniel Zavitz, is still working on his PhD thesis, which will be based on work done on this project. A second student, Chad Fulk, who was officially in the research group of Professor Sivananthan in our Physics Department worked on this project and some the work accomplished under this grant was included in his PhD thesis, which he successfully defended in March, 2007.

In one study [8] we sought to quantify and compare As coverages on Si(211) and Si(311) surfaces as well as Te coverages on the As/Si(211) and As/Si(311) surfaces. Results were obtained both in our laboratory and in UIC's Microphysics Laboratory (MPL). In our laboratory we had the ability to deposit As and transfer to our XPS spectrometer without exposure of the

samples to atmospheric pressure, whereas deposition and analysis were performed in different chambers in the MPL. *Ab Initio* calculations were performed in an attempt to establish the most stable surface structures and to identify the adsorption sites for As. In order to calibrate the results, As was also deposited onto the Si(111) surface.

The most significant publication from our laboratory concerned the influence of As on the atomic structure of the Si(211) surface [9]. In the introduction section of this paper we wrote a thorough review of the history of the epitaxial growth of HgCdTe on Si surfaces from MBE studies, the past LEED, STM, and other surface structural studies of the clean Si(211) surface, and of As deposition on Si(111) and Si(100) surfaces. To the best of our knowledge, there have not been previous studies of As on any high index Si surfaces. In this paper we showed XPS data establishing that we were able to deposit a monolayer of As onto clean Si surfaces without any observable contamination. We showed the highly reproducible LEED pattern of the clean Si(211) surface prepared in as similar a way as possible to the method used in MBE growth of CdTe. The LEED pattern shows the characteristic streaking associated with faceting. Finally, this paper presents STM images of the clean and As passivated Si(211) surface. The nanofacets present on the clean surface became much more regular on the As-passivated surface.

The third publication [10] involved an attempt to provide a more detailed analysis of the complex LEED pattern of the clean Si(211) surface. Although a structural model of clean Si(211) involving nanofacets was proposed by Baski, *et al.* [6] on the basis of STM images, no attempt had previously been made to rationalize the LEED pattern in terms of the nanofaceted structural model. Our paper showed how the streaky LEED pattern evolved to a more ordered pattern with sharper spots following annealing to temperatures above 1150° C. A detailed image of the STM image of the Si(211) surface was also presented that provided additional insight and support for the structural model proposed.

Collaborations

One of the original goals of the project was to foster interactions between groups directly involved in the MBE growth of HgCdTe on Si surfaces and our surface science group. These groups included researchers in the MPL at UIC, the Army Research Laboratory (ARL), and the Night Vision Laboratory (NVL) at Fort Belvoir. The interactions were pursued on various levels. A student from my group, Rasdip Singh, spent several months at ARL working with Drs. Gregory Brill and Nibir Dhar. While this had the benefit of making us aware of the issues of most interest to ARL, it had the unfortunate consequence of removing from my laboratory my most experienced and talented student. Although the MPL, NVL, and ARL groups had access to many surface analysis techniques, none had STM instrumentation or expertise. Thus, STM studies presented our best opportunity for making a unique contribution to the field. The location of our laboratory in the same building as the UIC MPL greatly facilitated interaction with students and other researchers associated with the MPL. Most significantly, Chad Fulk received his PhD in Physics based partly on work he did in my laboratory in collaboration with my group. In addition to interactions with ARL and NVL researchers at the annual II-VI Workshop, I made a trip to ARL and NVL in June, 2006. Among the researchers at these laboratories there was clearly a great deal of enthusiasm for the value of the work that we were doing and interest in establishing an even greater level of cooperation. In addition to these interactions, we also profited from interactions with Dr. Robert Sporken, a frequent visitor to the MPL from Belgium.

Future Directions

In addition to the instrumentation challenges described above, our efforts brought to light some unanticipated challenges. For example, the Si(211) surface is especially difficult to work with. Beautiful atomically-resolved images of the Si(111) and Si(100) surface are regularly obtained by many groups, including ours, with STM. For a variety of reasons, it is more difficult to obtain such high quality images on other silicon surfaces. Some high index Si surfaces are stable with respect to faceting, such as Si(311), whereas others, such as Si(211), are not. Although we might have achieved better images and reproducibility working with Si(311), it was clear that our MBE collaborators as well as other researchers working in this field were primarily interested in Si(211). To make our work as relevant as possible to the ultimate application, we tenaciously pursued STM work with Si(211). In retrospect, it would have been better to work on a less problematic surface. There are many issues common to all of the high index Si surfaces and from a fundamental perspective results of general value could have been derived from a simpler surface such as Si(311). In order to interpret our results for As-passivated Si(211), a more thorough understanding of As on Si(111) would have been useful. Even though there had been some earlier work on this problem, a side-by-side comparison of As/Si(211) and As/Si(111) would have been useful. Finally, before attempting to image CdTe thin films on Si surfaces, it would have been useful to have attempted STM on single crystals of CdTe itself. There is essentially no information on this topic in the literature. In retrospect, the best way to provide the information needed to assist the MBE researchers would have been to lay the groundwork by tackling more feasible problems first and then working up to the problems of most direct relevance to the applications. Of course, such a program would require stable funding with a longer term perspective. However, given that the first report of epitaxial growth of CdTe on a Si substrate was published almost 20 years ago [11], and that little progress has been achieved in obtaining a fundamental atomic scale understanding of the process, if a long-term approach had been adopted at the outset of this area of research, many of the problems would have probably been solved by now.

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